

STRUCTURE AND REACTIVITY OF TEXAS LIGNITE

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INTRODUCTION

The conversion of low rank coals such as lignites into gaseous and liquid fuels and chemical feed stocks received considerable attention in the last decade.¹⁻³ Data for liquefaction and gasification of various lignites have been reported.^{1,3-16} Although extensive analytical data are available on lignite conversion product, their use to monitor chemical reactions involved in any liquefaction or gasification process is limited due to the enormous amount of time and effort required for the complete characterization of Lignite conversion products.¹⁷⁻²¹ In the case of most of the reports on liquefaction experiments, the data are usually limited to total conversion, amount of certain fractions as oils, asphaltenes, preasphaltenes, tetrahydrofuran solubles, and certain physical characteristics.¹⁷ This study involves one lignite sample from a Texas mine and its conversion products from mini reactor experiments using varying liquefaction conditions. The gaseous products are analyzed by gas chromatography (GC)¹⁴ and the THF solubles are characterized by gel permeation chromatography (GPC)⁸⁻¹⁵ and high resolution gas chromatography (HRGC).

EXPERIMENTAL

Lignite samples were collected fresh from the mine near Carlos, Texas and stored under distilled water prior to use. The Lignite was ground to less than 20 mesh size and stored in a closed jar which was kept in the refrigerator. The lignite liquefaction experiments were conducted in four 6.3 ml mini reactors which were heated in a fluidized sand bath. The reactors were fabricated using 'Autoclave' fittings. Each reactor was the same, but only one reactor was fitted with a pressure transducer. The absence of pressure gauges on the other three reactors allowed the minimization of the dead volume outside the sand bath. In most cases 1.5 gm lignite, 1ml solvent (decalin or tetralin) and a gas (nitrogen or hydrogen or 1:1 CO/H₂ mixture at 1000 psi) were charges to the reactor. The reactions were quenched by dipping the reactors in cold water. The gases from the reactors were analyzed using an automated multi-column gas chromatograph equipped with sample injection and column switching valves.⁴ The contents of the reactors were extracted with tetrahydrofuran (THF) by using an ultrasonic bath. The THF extract (about 15 ml) was filtered through a 1 micron micro-pore filter (Millipore) and separated into fractions by using a gel permeation chromatograph (GPC).¹⁵

The GPC fractions were obtained with a Waters Associate Model ALC/GPC 202 liquid chromatograph equipped with a refractometer (Model R401). A Valvco valve injector was used to load about 100 μ l samples into the column. A 5 micron size 100 Å PL gel column (7.5 mm ID, 600 mm long) was used. Reagent grade THF, which was refluxed and distilled with sodium wire in a nitrogen atmosphere, was used as the GPC carrier solvent. A flow rate of 1 ml per

minute was used. THF was stored under dry nitrogen, and all separations were conducted in a nitrogen atmosphere to prevent the formation of peroxides.

Straight chain alkanes from Applied Science, aromatics from Fisher Scientific Company and polystyrene standards from Waters Associate were used without purification for the linear molecular size calibration of the GPC. Since the solubility of the larger alkanes in THF is very low, approximately 0.2-1 mg of each standard was dissolved in 100 μ l of THF for the molecular size calibrations. The fractions of the lignite derived liquid separated by GPC were analyzed by a gas chromatographic system (VISTA 44, Varian Associates) equipped with a 15 M long and 32 mm ID bonded phase fused silica capillary column and flame ionization detector.

RESULTS AND DISCUSSIONS

The lignite samples from Carlos, Texas have heating values of 4000 to 6000 BTU/lb on an as received basis or about 12000 BTU/lb on dry mineral matter free (dmmf) basis. The samples may contain as much as 40% moisture which escapes from lignite even while stored in the refrigerator (water condenses on the walls of the container). The oxygen content varied from 20 to 30 % and has about 1 to 1.5 % sulfur on a dmmf basis. As much as 50% of the oxygen may exist as carboxylic groups which may produce carbon dioxide at the liquefaction conditions.⁵ The substantial amount of hydrogen sulfide that was usually liberated, decreased rapidly as a function of sample ageing and storage conditions. The lignite seams are soaked with water under hydrostatic pressure in a virtually anaerobic condition. Immediately after mining, the lignite samples continuously loose moisture and are oxidized by air. There is no ideal way the lignite samples can be stored to preserve its on seam characteristics.

The lignite liquefaction conditions are listed in Table 1. The composition of gaseous products are listed in Table 2. The data in Table 2 illustrate that the composition of gaseous products are unaffected by reaction conditions such as reactor pressure, feed gas or the solvent system (whether hydrogen donating or not). Higher temperatures favor the production of hydrocarbons. Apparently the fragile species produced by the pyrolytic cleavages of bonds in the coal structure are converted to stabler species which form the components of lignite derives gases without consuming hydrogen from the gaseous phase or from the hydrogen donor solvents. The species which require hydrogen for stabilization are abstracting hydrogen from carbon atoms in the vicinity. It is quite possible that the bond breaking and hydrogen abstraction are simultaneous and hydrogen from the donor solvent or the gaseous phase may not reach the reaction site in time to hydrogenate the fragile species.

To illustrate the gaseous hydrocarbon production from lignite, experiments were conducted using butylatedhydroxytoluene (BHT), a widely used antioxidant and food preservative, as a model compound (see Table 1 & 2). BHT decomposed to products including isobutylene and isobutane in an approximate 1:1 molar ratio in the absence of hydrogen from hydrogen donor solvent or gaseous phase. Addition of tetralin favored the production of isobutane over isobutylene. It appears that coal lignite can give some hydrogen to the isobutane formation but tetralin can readily reach the reaction vicinity in time for the hydrogen transfer reaction.

The elution pattern of the GPC using 5 micron 100 Å PL gel column is illustrated in Figure 1 where the GPC separation of a standard mixture containing straight chain alkanes and aromatics is shown. The polystyrene standard (mol. wt. 2350 and chain length 57 Å) gave a broad peak at 11 ml retention volume. The peak position is marked in the figure rather than using polystyrene standard in the mixture in order to save the $nC_{44}H_{80}$ peak from the enveloping effect of the broad polystyrene peak. The retention volume of several aliphatic phenolic, heterocyclic, amine and aromatic compounds in THF and toluene have been reported elsewhere.⁹ It is clear that aromatic compounds, as expected from their valence bond structures, have smaller linear molecular sizes compared to n-alkanes of similar molecular weight.¹⁵ It is expected that most of the condensed ring aromatics such as naphthalene, anthracene and even big ones like coronene (seven fused rings with molecular weight of 300.4) are smaller than n-hexane and hence have retention volumes larger than that of n-hexane. The polystyrene standard with a 57 Å appears to be larger than expected from the alkane standard. The large number of phenyl groups on the main polyethylene chain (57 Å) make the molecule into a large cylindrical structure with large steric hinderance for penetrating the pores of the gel. The two terminal phenyl groups also contribute to an increased chain length. The polystyrene peak (57 Å) is very close to the total exclusion limit of the 100 Å PL gel column.

The THF solubles of lignite liquefaction products were separated by GPC on the basis of effective linear molecule sizes in solution.¹⁵ Although GPC can be used for molecular weight or molecular volume separation of homologous series such as polymers, such separations of complex mixtures like coal liquid is not feasible. The only molecular parameter which has the least variation from a calculated value is effective linear molecular size in solution. Lignite derived liquids are separated on the basis of effective molecular length which is expressed in carbon numbers of straight chain alkanes. The GPC fraction with species larger than $nC_{44}H_{80}$ is in fraction 1 which is composed of nonvolatile species. Fraction 2 has molecular sizes in the range of nC_{14} to nC_{44} and composed of volatile species mostly alkanes and nonvolatile species generally known as asphaltenes. Fraction 3 is composed of alkylated phenols such as cresols, alkyl indanols and alkyl naphthols as well as, some small amount of nonvolatiles namely low molecular weight asphaltenes. Fraction 4 is composed of species with molecular size less than that of $n-C_7H_{16}$. This fraction may not contain any straight chain alkanes as they are very volatile. It is composed of aromatic species such as alkylated benzenes, alkylated indans and naphthalene and even large species such as pyrenes and coronenes. The solvent system used for liquefaction (tetralin and decalin) separate from the bulk of the lignite derived products as the last peak (peak at 20.5 ml). Although the column is overloaded with respect to the solvent system, the efficiency of separation of the lignite derived products are unaffected. The volatile species of all fractions can be identified by GC-MS^{12,13,17} and nonvolatiles by the IR and NMR spectroscopy.

The effect of hydrogen donor solvent and feed gases such as hydrogen and CO/H_2 mixture on lignite dissolution at 700°F is shown in Figure 2. Decalin dissolves less coal compared to tetralin. CO/H_2 as feed gas gave less liquid products which contained more larger molecular size species. When decalin with nitrogen (not shown in Figure 2) was used for liquefaction of lignite the

species appearing at total size exclusion limit of 100 Å gel column were totally absent. Figure 3 shows GCs of fraction 2s of two lignite derived liquids to illustrate the role of the hydrogen donor solvent on alkane production. If the alkanes are formed by breaking of alkyl chains from other groups, they are expected to contain more olefinic species in the absence of hydrogen donor solvents such as tetralin. Since the species in figure 4 a and b are very similar, the role hydrogen or hydrogen donor solvent plays in the production of alkanes are limited. Simple pyrolysis can liberate them from the coal matrix. The alkane may be existing as free while trapped inside the pores or their precursors are either carboxylic acids or species which decompose during heating to produce alkanes easily.

Figure 4 illustrates the effect of reaction time on liquefaction. Figures 5 and 6 show the liquefaction of lignite at 750°F and 800°F using different feed gases. Hydrogen tends to give more phenols and aromatics compared to nitrogen. CO/H₂ tends to produce higher molecular size species at the expense of phenols and aromatics. A qualitative estimation of the solvent systems can be obtained estimating the width of the solvent peak, and the area of the rest of the GPC may give the dissolved product from lignite. The use of CO/H₂ did not increase the total liquefaction yield while it has decreased the total yield of liquid products. The experiments using CO/H₂ gave liquid product which are difficult to filter through micro pore filters compare to the products obtained from experiments using either nitrogen or hydrogen as the feed gas. It could be assumed that CO/H₂ will give a product which contained more large size asphaltenes.

Based on our data on lignite liquefaction products and various coal liquids and their distillates, we proposed a structure for coal as shown in figure 7. The major structural constituents of coal are derived from three sources namely cellulose, lignin and other plant components dispersed in the plant tissues. The first two are polymers. The coalification process which is mostly a deoxygenation process, might not create a sufficiently large number of tertiary bonds needed for binding various constituents of coal together to a strong three dimensional structure. The coals including lignite may have loose structures. The cellulose derived structures may have large pores in which species such as large alkanes could be trapped. Although low temperature (less than 300°F) extractions can extract some soluble components of coal, the alkanes are not liberated except as small amount of carboxylic acids. The low temperature oxidation studies do not detect large alkanes. The higher temperatures (above 650°F) can either break the pore structures or the alkanes can distill out of the pores.

ACKNOWLEDGEMENTS

The financial support of The Texas Engineering Experiment Station, The Texas A&M University Center for Energy and Mineral Resources, is very much appreciated. The lignite was supplied by TMPA, Carlos, Texas.

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Table 1. Lignite Liquefaction Conditions

Run No.	Coal g.	Solvent 1 ml	Feed Gas	Initial Pressure (psi)	Temp °F	Time min.	Comments
1	1.5	tetralin	N ₂	1000	700	30	+ BHT 0.2 g
2	1.5	tetralin	N ₂	1000	700	120	+ BHT 0.2 g
3	1.5	tetralin	N ₂	1000	700	120	
4	1.5	decalin	N ₂	1000	700	120	+ BHT 0.2 g
11	1.5	tetralin	CO+H ₂ (1:1)	1000	700	120	
12	1.5	tetralin	N ₂	1000	700	120	
13	1.5	decalin	N ₂	1000	700	120	
14	1.5 (old)	tetralin	N ₂	1000	700	120	
21	1.5	tetralin	N ₂	1000	700	120	
22	1.5	tetralin	no	0	700	120	+ BHT 1 g
23	1.5	no	no	0	700	120	
24	1.5 (old)	tetralin	N ₂	1000	700	120	
31	1.5	tetralin	H ₂	1000	700	120	
32	1.5	tetralin	CO+H ₂ (1:1)	1000	700	120	
33	1.5	decalin	H ₂	1000	700	120	
34	1.5	decalin	CO+H ₂	1000	700	120	
41	1.5	tetralin	N ₂	1000	700	15	
42	1.5	tetralin	N ₂	1000	700	120	
43	1.5	tetralin	N ₂	1000	700	360	
51	1.5	tetralin	N ₂	1000	850	30	
52	1.5	tetralin	H ₂	1000	850	30	
53	1.5	tetralin	CO+H ₂ (1:1)	1000	850	30	
61	1.5	tetralin	N ₂	1000	800	30	
62	1.5	tetralin	H ₂	1000	800	30	
63	1.5	tetralin	CO+H ₂ (1:1)	1000	800	30	
71	1.5	tetralin	N ₂	1000	750	30	
72	1.5	tetralin	H ₂	1000	750	30	
73	1.5	tetralin	CO+H ₂	1000	750	30	

TABLE II Composition of Product Gas %

Run No.	H ₂	CO ₂	CO	H ₂ S	CH ₄	C ₂	C ₂ ⁺	C ₃	C ₃ ⁺	n-C ₄	i-C ₄	i-C ₄ ⁺
1	13.0	11.2	26.1	-	8.4	1.3	1.9	0.8	0.15	0.07	12.6	24.1
2	2.1	61.5	3.6	-	9.2	2.8	2.8	1.8	0.23	0.19	11.9	5.9
3	0.9	80.0	0.9	-	11.8	3.7	7.3	1.2	0.13	0.17	0.1	0.03
4	0.3	61.9	2.1	-	8.6	2.0	1.5	1.0	0.10	0.07	8.7	13.2
11	3.2	60.4	2.5	22.4	6.8	2.6	0.2	1.0	0.12	0.14	0.1	0.01
12	3.7	70.5	2.8	10.5	7.9	2.6	0.3	1.0	0.14	0.15	0.1	0.1
13	0.5	75.9	3.8	7.8	8.4	2.2	0.6	0.6	0.10	0.06	0.04	0.02
14	2.3	78.2	2.9	1.1	9.7	3.4	1.2	1.1	0.10	0.13	0.1	0
21	1.1	80.7	1.5	-	9.5	2.6	0.3	1.5	0.15	0.16	1.8	0.8
22	5.2	51.2	3.4	-	28.1	3.6	0.04	3.2	0.01	0.06	3.9	0.9
23	-	76.5	3.6	-	11.4	3.9	0.2	2.0	0.31	0.41	0.2	0.1
24	0.8	83.7	1.6	-	8.3	3.1	0.3	1.2	0.18	0.17	0.1	0.03
31	0.7	71.3	2.7	13.1	7.3	2.6	0.7	0.9	0.12	0.18	0.2	0.2
32	0.7	70.1	1.9	12.7	5.3	1.8	0.4	0.6	0.10	0.09	0.1	0.1
33	0.7	75.5	2.1	11.3	7.3	1.9	0.1	0.7	0.12	0.07	0.1	0.03
34	0.8	63.0	2.4	-	19.1	4.2	1.1	2.2	1.64	0.90	1.3	1.1
41	-	80.8	2.1	11.5	3.9	0.8	0.3	0.2	0.09	0.03	0.03	0.03
42	1.0	74.3	1.5	10.2	7.5	3.2	0.8	1.1	0.13	0.15	0.1	0.02
43	5.6	41.2	1.3	37.1	9.2	3.7	0.1	1.4	0.11	-	0.1	0.01
51	8.8	44.7	4.7	8.8	21.0	5.5	0.4	2.2	0.26	0.44	0.2	-
52	8.1	46.6	5.3	7.6	23.2	6.6	0.4	1.7	0.23	0.17	0.1	0.02
53	9.9	47.5	5.4	9.9	19.0	5.5	0.1	1.8	0.24	0.29	0.2	-
61	1.7	65.8	6.0	9.4	11.1	4.3	1.2	0.1	0.23	0.21	0.1	0.03
62	1.6	65.8	6.0	8.8	11.8	3.9	0.6	1.0	0.16	0.11	0.1	0.02
63	1.6	66.1	5.9	10.4	11.5	3.2	0.1	0.9	0.14	0.09	0.1	0.02
71	0.7	78.4	3.7	4.9	8.3	2.4	0.4	0.7	0.14	0.11	0.1	0.03
72	0.7	76.9	2.4	6.6	9.2	2.9	0.1	0.8	0.14	0.10	0.1	0.02
73	0.7	75.2	2.9	8.7	8.0	2.8	0.5	0.8	0.16	0.10	0.1	0.02

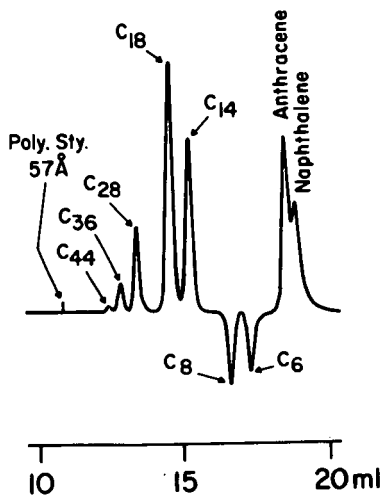


Figure 1. GPC of calibration mixture

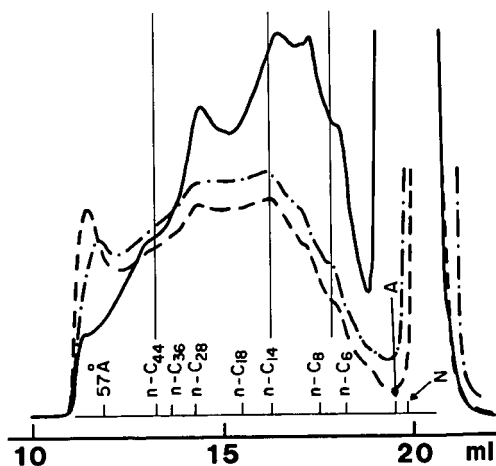


Figure 2. GPC of THF solubles of lignite from reactions at 700F in — decalin and H_2 (33), --- tetralin and H_2 (31) -- tetralin and CO/H_2 (32)

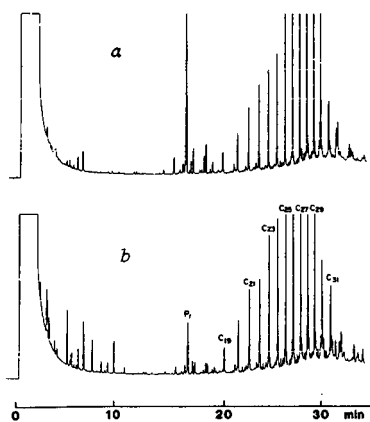


Figure 3. GC of alkane fractions from THF solubles of lignite a. tetralin and H_2 (21) b. Decalin and N_2 (13)

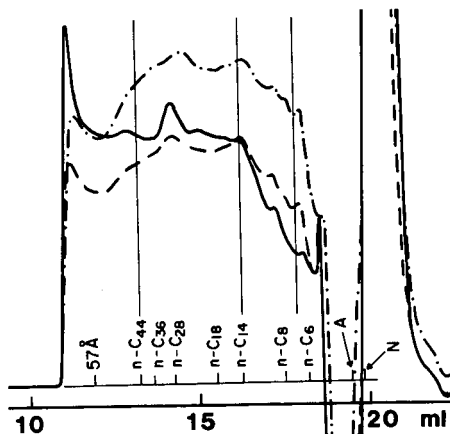


Figure 4. Effect of reaction time on THF solubles of lignite in tetralin and H_2 at 700F. — 15 min. (41), --- 120 min. (42), -- 360 min. (43)

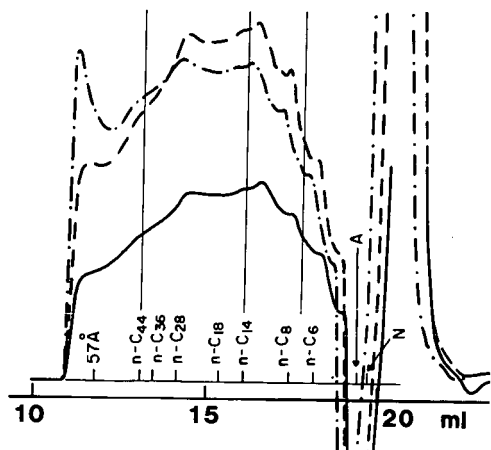


Figure 5. Effect of feed gas on lignite liquefaction in tetralin at 750 F — N_2 (71), --- H_2 (72), -.- CO/H_2 (73)

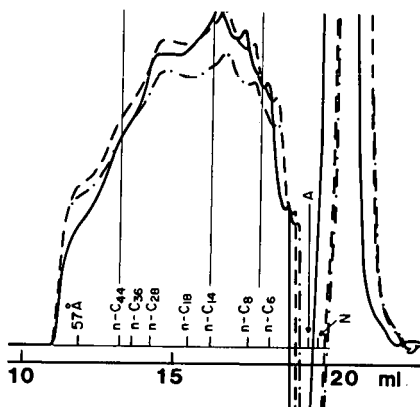


Figure 6. Effect of feed gas on lignite liquefaction in tetralin at 800 F. — N_2 (61), --- H_2 (62), -.- CO/H_2 (63)

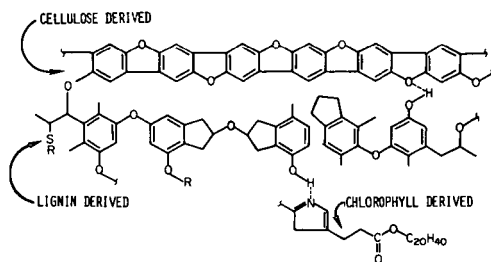


Figure 7. A structural model of coal